MEAN AMPLITUDES OF VIBRATION: BENT XYZ MOLECULES

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Abstract

The theory of mean-square amplitude matrices is applied to the bent XYZ molecules. The principal mean amplitudes of vibration for the molecules investigated here are reported for 300° K.

Introduction

The study of mean amplitudes of vibration is of great interest for electron diffraction investigations. It provides an additional set of parameters required in defining the nonrigid model of the molecules. It serves as an additional information to normal frequencies in the determination of a complete harmonic force field. The theory of computing the mean amplitudes of vibration from spectroscopic data is developed by Morino and Hirota.[1] A slightly modified method is suggested by Cyvin,[2] who gave a new secular equation, relating the mean-square amplitudes of vibration to the normal frequencies. In this investigation, Cyvin's method has been applied to the evaluation of mean amplitudes of ten bent XYZ molecules at 300° K. using their vibrational frequencies. All the bonded and nonbonded mean square amplitude quantities and the corresponding mean amplitude quantities of these molecules are reported here for the first time.

2. Symmetry Co-ordinates

The bent XYZ molecules (Fig. 1) belong to the point group C_s and possess three A′ normal modes of vibration.

The following are the symmetry co-ordinates formed out of the valence force co-ordinates $\triangle D$, $\triangle R$ and $\triangle \alpha$, where D, R and α denote the equilibrium values.

$$S_1 = \triangle D$$

$$S_2 = \triangle R$$

$$S_3 = (DR)^{\frac{1}{2}} \triangle \alpha.$$

The angle displacement co-ordinate has been multiplied by $(DR)^{\frac{1}{2}}$ in order to have the same dimension to all the symmetry co-ordinates.
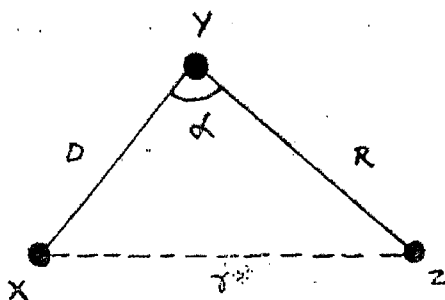

FIG. 1. Configuration of bent XYZ molecules.

3. SYMMETRIZED MEAN-SQUARE AMPLITUDE MATRIX

The harmonic potential energy function for XYZ molecules is given below in terms of the valence force co-ordinates.

$$2V = f_D (\triangle D)^2 + f_R (\triangle R)^2 + f_\alpha (\triangle \alpha)^2 + 2f_{DR} (\triangle D)(\triangle R)$$

$$+ 2f_{D\alpha} (\triangle D) (D\alpha) + 2f_{R\alpha} (\triangle R) (\triangle \alpha).$$

Where f_D and f_R are the XY and YZ stretching constants respectively, f_α the bending constant and f_{DR}, $f_{D\alpha}$, $f_{R\alpha}$ are the interaction constants concerning the respective parameters.

Using the above potential function, the symmetrized mean-square amplitude matrix Σ is formed and the elements of Σ matrix are given below in terms of the symmetry co-ordinates.

$$\Sigma_{11} = \langle S_1{}^2 \rangle = \sigma_D$$

$$\Sigma_{22} = \langle S_2{}^2 \rangle = \sigma_R$$

$$\Sigma_{33} = \langle S_3{}^2 \rangle = \sigma_\alpha$$

$$\Sigma_{12} = \langle S_1 S_2 \rangle = \sigma_{DR}$$

$$\Sigma_{13} = \langle S_1 S_3 \rangle = \sigma_{D\alpha}$$

$$\Sigma_{23} = \langle S_2 S_3 \rangle = \sigma_{R\alpha}$$

4. ADDITIONAL MEAN-SQUARE AMPLITUDE

Considering the nonbonded distance deviation $\triangle r^*$, the following additional mean-square amplitude quantity is obtained in terms of the symmetrized mean-square amplitude matrix elements.

$$\sigma_{T^*} = \langle (\triangle r^*)^2 \rangle$$

$$= \frac{1}{r^{*2}} [A^2 \sigma_D + B^2 \sigma_R + C^2 \sigma_\alpha + 2AB\sigma_{DR} + 2BC\sigma_{R\alpha} + 2AC\sigma_{D\alpha}].$$

Where r^* is the interatomic displacement between nonbonded atoms, $A = (D - R \cos \alpha)$, $B = (R - D \cos \alpha)$, $C = (DR)^{\frac{1}{2}} \sin \alpha$ and $r^* = (D^2 + R^2 - 2DR \cos \alpha)^{\frac{1}{2}}$.

5. G MATRIX

Using Wilson's method the following G matrix elements are obtained:

$$G_{11} = \mu_X + \mu_Y$$

$$G_{22} = \mu_Z + \mu_Y$$

$$G_{33} = DR \left[\frac{\mu_X}{D^2} + \frac{\mu_Z}{R^2} \right] + (DR) \frac{\mu_Y}{\sin^2\alpha} \left[\left(\frac{1}{R} - \frac{\cos \alpha}{D} \right)^2 \right.$$
$$\left. + \left(\frac{1}{D} - \frac{\cos \alpha}{R} \right)^2 + 2 \left(\frac{1}{R} - \frac{\cos \alpha}{D} \right) \left(\frac{1}{D} - \frac{\cos \alpha}{R} \right) \cos \alpha \right]$$

$$G_{12} = \mu_Y \cos \alpha$$

$$G_{13} = - (DR)^{\frac{1}{2}} \frac{\mu_Y}{\sin \alpha} \left[\left(\frac{1}{R} - \frac{\cos \alpha}{D} \right) + \left(\frac{1}{D} - \frac{\cos \alpha}{R} \right) \cos \alpha \right]$$

$$G_{23} = - (DR)^{\frac{1}{2}} \frac{\mu_Y}{\sin \alpha} \left[\left(\frac{1}{D} - \frac{\cos \alpha}{R} \right) + \left(\frac{1}{R} - \frac{\cos \alpha}{D} \right) \cos \alpha \right].$$

6. RESULTS AND DISCUSSION

The elements of the mean-square amplitude matrix Σ were obtained by solving the secular equation

$$| \Sigma G^{-1} - E\triangle | = 0$$

where G^{-1} is the inverse of the kinetic energy matrix and E is the unit Matrix. The values of $\triangle$ are connected with the normal frequencies ν_k by the relation

$$\Delta_k = \frac{h}{8\pi^2 v_k} \; \text{coth} \left(\frac{h v_k}{2kT} \right)$$

where h is the Planck's constant, k is the Boltzmann's constant and T absolute temperature.

The molecular parameters and the observed fundamental frequencies of the molecules studied in this investigation are given in Table I.

The mean-square amplitudes of vibration evaluated for the bonded and nonbonded distances respectively are listed in Table II.

The mean amplitude quantities, $\sigma_D{}^{\frac{1}{2}}$, $\sigma_R{}^{\frac{1}{2}}$ and $\sigma_{r*}{}^{\frac{1}{2}}$, are given in Table III.

It can be seen from the results presented in Table III that the mean amplitudes of vibration for some bonded interatomic distances are found to possess characteristic values, namely, nearly 0·0695 for OH bond in HDO and HOCl molecules and 0·04226 for N = O bond in the nitrosyl compounds. The mean amplitude values for nitrogen halogen bond in nitrosyl compounds increase from lower to higher members of the series and the same trend is noted for the oxygen-halogen nonbonded distances also but the increase is more rapid in the case of nonbonded mean amplitudes.

TABLE I

Molecular parameters and observed frequencies $(cm.^{-1})$ of bent XYZ molecules

Molecules	Bond angle	Bond length		Observed frequencies			References
		D Å	R Å	ν_1	ν_2	ν_3	
DOH	104° 31′	0·958	0·958	2727	1402	3707	3, 4
DSH	92°	1·345	1·345	1078	2585	2619	5, 6
DSeH	91°	1·47	1·47	1691	905	2352	7, 8
$O^{16}SO^{18}$	120°	1·46	1·46	1122	507	1341	9, 10
HOCl	113°	0·957	1·7	3626	1242	739	11, 11
DOCl	113°	0·957	1·7	2674	911	739	11, 11
ONF	110°	1·13	1·52	1844	521	766	12, 13
$ON^{15}Cl$	116°	1·14	1·95	1760	331	590	14, 15
$ON^{14}Cl$	116°	1·14	1·95	1800	332	605	14, 16
ONBr	117°	1·15	2·14	1801	265	542	14, 16

TABLE II

Mean-square amplitudes ($Å^2$) of bent XYZ molecules at 300° K.

Molecules	Mean square amplitudes			
	σ_{ν}	σ_R	σ_{α}	σ_r*
DOH	0·003373	0·004884	0·019351	0·013321
DSH	0·004145	0·005663	0·031172	0·014034
DSeH	0·005188	0·007268	0·027283	0·020198
$O^{16}SO^{18}$	0·001561	0·001432	0·006419	0·009091
HOCl	0·004801	0·001748	0·038193	0·010543
DOCl	0·004661	0·001748	0·020324	0·007285
ONF	0·001786	0·003249	0·010122	0·003345
$ON^{15}Cl$	0·001579	0·003215	0·013491	0·004272
$ON^{14}Cl$	0·001786	0·003311	0·013934	0·005148
ONBr	0·001788	0·003481	0·014582	0·006061

TABLE III

Mean amplitudes ($Å$) of bent XYZ molecules at 300° K.

Distance / Molecule	(X — Y)	(Y — Z)	(X···Z)
DOH	0·05808	0·06988	0·11661
DSH	0·06512	0·07518	0·11842
DSeH	0·07202	0·08526	0·14211
$O^{16}SO^{18}$	0·03951	0·03785	0·09535
HOCl	0·06929	0·04184	0·10269
DOCl	0·06828	0·04184	0·08525
ONF	0·04226	0·05701	0·05784
$ON^{15}Cl$	0·03973	0·05671	0·06536
$ON^{14}Cl$	0·04226	0·05754	0·07176
ONBr	0·04229	0·05899	0·07785

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